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DEVELOPMENT OF A MOLTEN CARBONATE PROCESS FOR REMOVAL OF SULFUR DIOXIDE FROM POWER PLANT STACK GASES

PROGRESS REPORT NUMBER 2
PART V. FLY ASH STUDIES
April 1, 1968 to October 27, 1968

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FLY ASH IN THE ATOMICS INTERNATIONAL MOLTEN CARBONATE PROCESS: PHYSICAL PROPERTIES AND FILTRATION CHARACTERISTICS

SUMMARY

The Atomics International Molten Carbonate Process is based on the use of molten carbonate salts to remove sulfur dioxide and last traces of fly ash from flue gases. The salt stream is regenerated and recycled. It follows that fly ash must be continually removed from the molten salts, or it will accumulate and finally render the liquid salt to a paste. This report describes investigations of the physical properties of fly ash and methods for filtering the ash from suspension in molten salts.

Fly ash particle density was found to be close to that of the molten eutectic of lithium, sodium and potassium carbonates; $\rho_{liq}(450°C) = 1.97$ gm/cm^3. Mean particle densities were measured at 2.06, 2.11 and 1.96 cm/cm^3 for three different coal fly ashes. The bulk density of coal fly ash is of the order of 0.9 gm/cm^3; that of oil soot is about 0.2 gm/cm^3.

Fly ash porosity is about 50% for dry coal ash; the porosity of dry oil soot is greater, about 90%. The porosity of melt-saturated coal ash, about 67%, appears to be greater than that of the dry ash.

While water was found to leach approximately 6 wt % of coal fly ash, sulfuric acid at concentrations of 1 to 50 wt % leached about 20% of coal fly ash.

Fortunately, coal fly ash is very sparingly soluble in the carbonate eutectic melt. The only constituents which dissolve to any extent in the melt are the oxides of calcium and iron; solubilities are respectively 0.22 and 0.18 g metal/100 g melt at 450°C.

Fly ash can be filtered from suspension in carbonate with a sintered-metal medium. The filtrate obtained from passing a 1.5 wt % ash suspension through a commercial filter with 10 micron pores contained less than 0.003 wt % fly ash. The pressure drop across the filter was attributable primarily to flow resistance of the filter cake. The cake contained 67 wt % (or 67 vol %) carbonate.

I. INTRODUCTION

A. THE ORIGIN OF FLY ASH

Native coal contains up to 15% of metal oxides. When coal is pulverized and fired in a boiler, these oxides become airborne in the flue gas as fly ash. Any ash in the form of slag or clinkers is termed bottom ash.

Fly ash is a very fine powder and does not readily settle from the air by gravity. Unless it is collected from the flue gas, fly ash blows out the boiler plant stack as a plume and finally falls to earth as a dirt and nuisance. Power plants generally employ ash collection devices which remove between 50 and 95% of the ash in flue gas. The remainder exits to the atmosphere.

B. THE MOLTEN CARBONATE PROCESS

In the Atomics International Molten Carbonate Process, boiler flue gas is contacted with liquid carbonate salts to abosrb sulfur dioxide. All gas leaving the boiler is thoroughly scrubbed with the molten salt.

Fly ash in the gas stream will also be scrubbed by the liquid salt. Should fly ash accumulate in the recirculating salt, the suspension would thicken to a slurry, finally to a rigid paste. It is then evident that fly ash which becomes suspended in the molten salts must be continuously removed.

C. PURPOSE OF THIS INVESTIGATION

The primary purpose of this study has been to develop a method for removing fly ash from suspension in molten salts. Other goals have been to study the effect of fly ash upon the chemistry and mechanics of the Molten Carbonate

Process and to characterize the properties of fly ash and fly ash suspensions.

II. PHYSICAL PROPERTIES OF FLY ASH

A. THE CHARACTER OF FLY ASH

Bulk fly ash from coal-fired boilers is a talc-like powder, usually light gray in color. A tan color is usually associated with presence of iron oxide. Darker colors are associated with carbon or magnetic iron oxide. The bulk ash is dusty. Bulk fly ash from oil-fired boilers, usually called soot, is a fluffy powder, very black due to its carbon content.

Brackett [1] reports that individual particles of coal fly ash range in size from less than 1 micron to about 80 microns, the smaller particles being hollow, translucent spheres. He describes carbonaceous particles to range in shape from slivers to spongy or lace-like entities ranging in size from 10 to sometimes 300 microns. Katz [2] typifies the fly ash from pulverized coal as ranging between 0.1 and 80 microns with median diameter of 40 microns.

B. PARTICLE SIZE DISTRIBUTION

The size of an irregular particle requires careful description. In this report particle size or particle diameter refers to that determined by sieving.

Particle size distributions for fly ashes were received from several power stations. Figure 1 shows size distribution curves for Detroit Edison fly ash leaving the boiler and two samples of airborne dust emitted from the ash precipitator. The curves show that the particle diameters are log-normally distributed with the following percentile sizes.

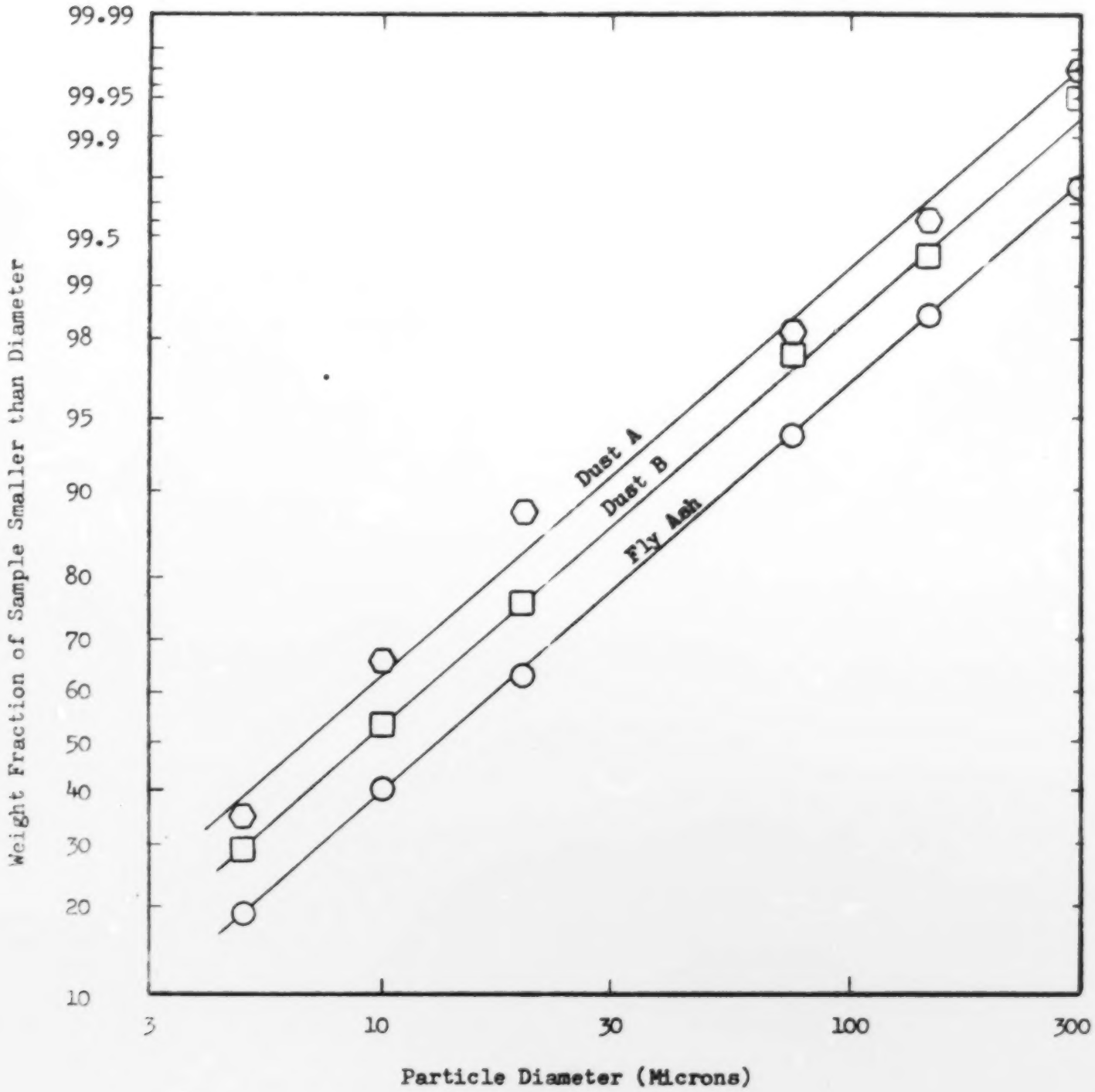

Figure 1. Cumulative Plot of the Size Distribution Data for Dust and Fly Ash From Detroit Edison Company

TABLE 1

PARTICLE SIZE DISTRIBUTION OF DETROIT EDISON FLY ASH

	Fly Ash (μ)	Dust A (μ)	Dust B (μ)
10% by weight smaller than	3.2	(1.7)*	(2.2)
50% by weight smaller than	13	7.1	9.3
95% by weight smaller than	84	43	59
99% by weight smaller than	178	89	124

*Parentheses indicate a value estimated by extrapolation.

The mass median particle diameters of several other fly ashes are listed in Table 2.

TABLE 2

MASS MEDIAN PARTICLE DIAMETERS D_g OF SEVERAL FLY ASHES

Source	D_g (μ)
Public Service of Colorado	
Cherokee Unit No. 1	
Mechanical collector inlet	33
Mechanical collector outlet	28
Arapahoe Unit No. 2	
1964	
Mechanical collector outlet	7
Mechanical collector hopper	18
1967	
Mechanical collector outlet	< 5
1968 collector outlet	4

TABLE 2

MASS MEDIAN PARTICLE DIAMETERS D_g OF SEVERAL FLY ASHES
(continued)

Source	D_g (μ)
Arapahoe Unit No. 3	
1964	
Mechanical collector inlet	12
Mechanical collector outlet	10
1966 collector inlet	< 5
1966 collector outlet	< 5
Four Corners of Arizona	
Mechanical collector inlet	19
Mechanical collector hopper	24
Mechanical collector outlet	4

One concludes from these data that mean fly ash particle size varies widely between stations and times of sampling at the same station.

C. CHEMICAL COMPOSITION

The distribution of chemical species in fly ash is variable. The ranges of ash compositions from eleven ash samples sent to AI are listed in Table 3.

TABLE 3

RANGES OF COMPOSITION FOR ELEVEN FLY ASH SAMPLES

SiO_2	32	to	53 wt %
Al_2O_3	16	to	35 wt %
CaO	4	to	30 wt %
Fe_2O_3	4	to	12 wt %
MgO	0.1	to	4 wt %
TiO_2	0.9	to	1.2 wt %

The oxides of many other metals are present in trace amounts.

D. DENSITY

1. Particle Density

The density of fly ash particles determines whether the ash will sink or float in molten salts and in an important variable in centrifugal removal of ash from melts.

Since fly ash consists of irregular particles containing pores and enclosed chambers, the measured density of fly ash particles is less than the theoretical density calculated from the densities of the individual constituents. The density of fly ash particles was estimated (*) by measuring the volume of water displaced by a known mass of fly ash. The estimated particle densities of several fly ashes are listed in Table 4.

*"Estimate" is used here in place of the more general "measured" or "determine". Since there was variability among several replicate observations of fly ash density, the true density is estimated by the sample mean.

TABLE 5

MEASURED BULK DENSITIES OF FLY ASHES

Fly Ash	Mean Bulk Density (gm/cm^3)	90% Confidence Limits of Mean, (gm/cm^3)
Public Service of Colorado, #1 Boiler	0.977	± 0.004
Consolidation Coal	0.85	± 0.00
Four Corners, Arizona	0.99	± 0.01
Scattergood, #1 Boiler (oil)	0.187	± 0.02
Scattergood, #2 Boiler (oil)	0.20	± 0.00

The variability in bulk porosity among types of ash is associated with the fact that some ashes are compact powders while others are light and fluffy.

E. POROSITY OF FLY ASH

Porosity is defined as the fraction of voids or non-solids in a bulk volume of porous solid. It is necessary to define the state of fly ash when considering porosity; the porosities of dry ash, ash saturated with water, and with molten salts are expected to differ.

In preliminary experiments, the porosity of water-saturated fly ash was measured by water displacement. Sample means for observations of porosity of water-saturated fly ash are listed in Table 6.

TABLE 4

PARTICLE DENSITIES OF SEVERAL FLY ASHES

Source	Mean Density (g/cc)	95% Confidence Interval (*)
Public Service of Colorado #1	2.06	1.93 - 2.19
Consolidation Coal	2.11	2.09 - 2.13
Four Corners of Arizona	1.96	1.85 - 2.07
Scattergood #1 (oil fired)	2.22	1.84 - 2.60
Scattergood #2 (oil fired)	1.96	1.85 - 2.07

*The confidence interval is interpreted as "in collecting 100 samples of N replicates each, the true particle density will fall within the confidence interval 95 times."

If centrifuges are used to separate fly ash from suspension in molten salts, it is necessary that the ash be more dense than the salt melt. The data in Table 4 show that ash density is close to melt density. However, in allowing suspensions of fly ash in molten carbonate ($\rho_{liq}(450°C) = 1.97\ g/cm^3$) to separate by gravity the ash has always sunk.

2. Bulk Density

Bulk density is the mass to volume ratio of bulk ash; for example, the kilograms of bulk ash contained in a one-liter beaker.

The measured bulk densities of several fly ashes are listed in Table 5.

TABLE 6

POROSITIES OF SEVERAL FLY ASHES SATURATED WITH WATER

Source	Mean Porosity
Public Service of Colorado Boiler #1	0.447
Consolidation Coal	0.527
Four Corners, Arizona	0.517
Scattergood, Boiler #1 (oil)	0.888
Scattergood, Boiler #2 (oil)	0.893

The porosity of fly ash saturated with molten salt is important in describing the properties and percent salt retention of an ash-melt filter cake. The porosity of an ash-melt cake retained on a sintered-metal filter was measured by freezing the cake and assaying samples for percent ash and percent carbonate.

Pieces of frozen filter cake, chipped from the sintered-metal filter medium, were powdered and split into two halves. The carbonate from one-half was dissolved in 1% aqueous H_2SO_4. The remaining solids were washed, filtered on a Millipore filter, dried and weighed. The other half of the powdered cake was assayed for percent metal carbonate by acidifying the powder and measuring the amount of evolved carbon dioxide with a gas chromatograph.

Results of these assays showed:

% M_2CO_3 in cake	66.8 wt %
% fly ash in cake	28.7 wt %
Total	95.5 wt %

Accordingly, the porosity of melt-saturated fly ash is estimated to be of the order of 67%.

F. SOLUBILITY OF FLY ASH IN MOLTEN SALTS, ACID, AND WATER

1. Introduction

Were fly ash to dissolve freely in molten salt, one would expect the physical properties of the melt (e.g. viscosity, surface tension, melting point) to alter. Moreover, certain elements, if readily soluble, could accumulate to change the chemical properties of the melt. An example of this is iron, which catalyzes the reduction reaction. Of course, insoluble compounds will be removed continuously in the melt filter.

2. Fraction of Fly Ash Leached by Sulfuric Acid and Water

In a proposed process for recovering lithium salts from fly ash-carbonate filter cake, and in analytical techniques, fly ash is suspended in sulfuric acid solutions. To estimate the extent of ash dissolution in such processes, the fraction of fly ash leached by aqueous sulfuric acid was measured.

One gram of Public Service of Colorado #1 fly ash was added to 100.00 ml of aqueous H_2SO_4. The suspension was agitated for 10 minutes, left for 20 hours, then filtered. The dried filter cake was weighed, giving a value for the fly ash fraction soluble in acid. The averaged results are listed in Table 7.

TABLE 7

SOLUBILITY OF FLY ASH IN SULFURIC ACID

Wt % H_2SO_4	Percent of Fly Ash Dissolved
0	5.7
1	17.0
7	25.3
50	18.7

3. Solubility of Fly Ash in Absorber-Effluent and Reducer-Effluent Melts

This study was made to measure the solubilities of fly ash components in sulfate-bearing and sulfide-bearing carbonate melts.

a. Apparatus and Procedure

1000 g of a mixture of 37 weight percent M_2CO_3 and 63 weight percent M_2SO_4 was melted in a graphite crucible. The melt, held at 850°F, was typical of absorber effluent and samples from this mixture are denoted with the prefix "a".

Five weight percent of Public Service of Colorado #1 fly ash was added to the system. The ash-melt mixture was agitated three times at one-half hour intervals and two 30 ml volumes (a1CRUC and a2CRUC) were collected from the homogeneous ash-melt mixture in the crucible. Then after the mixture had settled for one hour to allow gravity separation of larger ash particles, two 30 ml volumes of melt were collected near the liquid surface.

Each 30 ml volume collected at the melt surface was filtered through a sintered-metal filter with nominal ten-micron openings. The two filter cakes were scraped from the filter giving the sample a1CAKE and a2CAKE. The two filtrates were solidified, powdered, and quartered giving the sample a1FILT and a2FILT.

The above steps were repeated with a salt mixture of 75 wt % M_2CO_3 and 25 wt % M_2S typical of reducer effluent in the molten carbonate process. Samples from this mixture were denoted with the prefix "r".

All samples were assayed by emission spectroscopy for prevalent metals.

b. Results

The results of the emission spectroscopy assay are listed in Table 8. below. All quantities are in parts per million. The first column of Table 8. (CRUC) lists the cation concentrations observed in the homogeneous suspension samples taken before settling and filtration. The next two columns, (CAKE) and (FILT) list the cation concentrations of the filter cake and filtrate respectively from the samples collected after the ash had been allowed to settle out. The last column shows the concentrations of cations in dry fly ash.

TABLE 8

RESULTS OF EMISSION SPECTROSCOPIC ANALYSIS OF SALT SAMPLES
(Values listed are concentrations of cations in ppm)

Sample	Metal	Suspension in Crucible (CRUC) (Homogeneous)	Filter Cake (CAKE)	Filtrate (FILT)	Fly Ash (ppm)
a1	Ca	3,000	500	100	65,000
	Fe	1,000	4,000	150	25,000
	Si	10,000	10,000	< 10	265,000
	Al	10,000	10,000	< 10	85,000
	Mg	500	500	100	50,000
	Cr	-	600	10	75
	Ni	-	300	20	300
a2	Ca	3,000	750	750	65,000
	Fe	2,000	10,000	300	25,000
	Si	10,000	9,000	< 10	265,000
	Al	10,000	> 15,000	< 10	85,000
	Mg	1,000	600	60	50,000
	Cr	-	2,000	< 10	75
	Ni	-	2,000	30	300
r1	Ca	3,000	750	750	65,000
	Fe	1,000	> 10,000	7,500	25,000
	Si	10,000	3,000	500	265,000
	Al	10,000	50	< 10	85,000
	Mg	500	30	10	50,000
	Cr	10,000	10,000	200	75
	Ni	-	10,000	5,000	300
r2	Ca	3,000	750	750	65,000
	Fe	1,000	> 10,000	9,000	25,000
	Si	10,000	4,000	750	265,000
	Al	10,000	300	< 10	85,000
	Mg	750	10	< 10	50,000
	Cr	-	9,000	75	75
	Ni	-	7,500	2,000	300

c. Discussion

(1) Errors

In the following discussion, a sample refers to two replications *1*** and *2***, say r1CAKE and r2CAKE.

Variations among the four CRUC compositions - all CRUC compositions should be the same - are less than composition variations between a and r samples (e.g. a1CAKE and r2CAKE). Similarly, variations among the CRUC assays are less than variations between composition treatments, that is, the composition of a1FILT varies markedly from the composition of r1FILT, while the compositions of a1CRUC and r1CRUC are quite similar. The CRUC samples then serve as a control and are an indication of within-sample error due to both natural variation and assay variation. It is seen that the error in measurement is small enough to allow comparison between treatments.

(2) Fly Ash Solubility in the Absorber Melt

Compositions of a1**** and a2**** can be averaged because they are replicates of a single sample. Comparison of averaged compositions of the CAKE and FILT samples indicates that silicon, aluminum, magnesium, chromium, and nickel compounds are virtually insoluble in the absorber melt and that they may be removed from the melt with a sintered-metal filter. In addition, the metals comprising the 316 SS filter are not appreciably leached by a single pass through the filter.

On the other hand, both calcium and iron compounds were found in the filtrate. Calcium and iron compounds probably passed through the filter

in solution. The possibility that calcium and iron compounds passed the filter as micron-sized particles is remote because particles of other compounds were stopped.

In later experiments involving only pure calcium oxide and pure iron oxide in carbonate-sulfate melts, higher solubilities of calcium and iron were observed. The lower solubilities observed in these tests may have been due to (i) the unavailability of calcium and iron oxides in the interiors of fly ash particles causing the solution to be unsaturated, or (ii) calcium and iron being present in the fly ash as silicates which are probably less soluble than the oxides.

The mean concentration of iron found in the filtered absorber melt, 225 ppm or 0.025%, is too low to have any appreciable catalytic effect upon the reduction reaction.

(3) Fly Ash Solubility in the Reducer Melt

From inspection of the data showing concentrations of cations in the filtrate (Table 8), it is immediately evident that presence of the sulfide ion greatly increases the solubility of several fly ash components, notably iron, silicon, chromium, and nickel.

The solubility of iron, about 225 ppm in the absorber melt, increased to about 8250 ppm in the sulfide-bearing reducer melt. In a separate study [3], solubility of 7,400 ppm in a melt of 12.3 wt % H_2S was reported. This agrees with the observation in this study of 7,500 to 9,000 ppm Fe dissolved in a sulfide-bearing melt.

The results do not reveal a change in the solubility of calcium compounds with the change in melt composition. The mean solubilities of 425 and 750 ppm Ca of respective samples from the absorber and reducer melts are not significantly different at the 10% level of significance.

The chromium and nickel found in the filtrate at about 140 and 3,500 ppm respectively, were evidently leached from the sintered-metal filter medium. Their concentrations in the fly ash of 70 and 300 ppm respectively, would have allowed only 4 and 15 ppm respectively in the melt.

Aluminum and magnesium were virtually insoluble in both melts.

Silicon, insoluble in the absorber melt, dissolved at about 625 ppm in the sulfide-containing reducer melt.

4. Solubilities of Pure Fe_2O_3 and CaO in Sulfate-Carbonate Melts.

In earlier fly ash solubility studies, it was learned that the compounds of iron and calcium were the most soluble in carbonate-sulfate (M_2CO_3-M_2SO_4) melts. This test was conducted to determine more accurately the solubility of iron and calcium compounds.

a. Apparatus and Procedure

(1) Fe_2O_3 Solubility

To a very clean graphite crucible, the following were added:

210 g Li_2CO_3	123.3 g $Li_2SO_4 \cdot H_2O$
210 g $K_2CO_3 \cdot 1\frac{1}{2} H_2O$	123.3 g K_2SO_4
210 g Na_2CO_3	123.3 g Na_2SO_4 ,

which on heating to 860°F lost 52 g of water of hydration to give a 948.1 gram mixture of 62.3 wt % M_2CO_3 and 37.2 wt % M_2SO_4. 100 grams of Fe_2O_3 was then

added and the mixture was stirred at hourly intervals during the day. It was allowed to settle overnight and samples were taken the following morning (24 hours after addition of Fe_2O_3). A second set of samples was taken 24 hours later.

(2) CaO Solubility

To an identical carbonate-sulfate salt mixture, 10 grams of calcium oxide were added and the same procedure as before was followed. Samples were taken only 24 hours after addition of calcium oxide.

b. Results

The samples collected were assayed for iron by a colorimetric method and for calcium by a volumetric method. Results of the assay are listed in Table 9.

The color of the cooled and frozen melt is noted under Sample Color. The last two columns of Table 9 give the same cation solubility information, but in different units: wt % metal is grams of metal per 100 grams of metal-oxide-melt mixture, an engineer's unit; g metal/100 grams (metal-oxide-free) melt is the chemist's unit of solubility.

TABLE 9

METAL CONTENTS OF SALT SAMPLE IN SOLUBILITY STUDIES

Sample No.	Sample Color	Location of Sample Collection	wt % Fe	$\frac{g\ Fe}{100\ g\ melt}$
		Fe_2O_3 24 Hour Samples		
24 Fe 1 T	White	1 in. below surface of melt	0.19	0.19
24 Fe 2 T	Pink	1 in. below surface of melt	3.65	3.85
24 Fe 3 T	Red	1 in. below surface of melt	5.32	5.77
24 Fe 4 T	Red	1 in. below surface of melt	6.06	6.65
		Fe_2O_3 48 Hour Samples		
48 Fe 1 T	White	1 in. below surface of melt	0.18	0.18
48 Fe 2 T	Red	1 in. below surface of melt	4.59	4.80
48 Fe 3 T	Red	1 in. below surface of melt	5.98	6.56
48 Fe 4 T	Red	1 in. below surface of melt	8.06	8.85
		CaO 24 Hour Samples	% Ca	$\frac{g\ Ca}{100\ g\ melt}$
24 Ca 1 T	White	1 in. below surface of melt	0.22	0.22
24 Ca 2 T	White	1 in. below surface of melt	0.36	0.36
24 Ca 3 B	White	1 in. above bottom	0.43	0.43
24 Ca 4 B	White	1 in. above bottom	1.05	1.07

c. Discussion

In the Fe_2O_3 test only the white-colored samples could be considered valid; the red samples contained undissolved Fe_2O_3. There was no significant change in Fe concentration between 24 and 48 hours and the melt was considered saturated with Fe_2O_3 after 24 hours.

Calcium oxide concentration values may have included undissolved CaO. Presence of undissolved CaO was impossible to detect visually as all the samples were white in color.

Settling had occurred in the crucible. The mean concentration of calcium near the bottom of the crucible, 0.74%, was not significantly different from the homogeneous concentration of 0.72% (10 g CaO in 948.1 g melt). However, the mean concentration of calcium at the top of the crucible, 0.29%, was significantly different from the mean concentration, 0.72%, in a statistical t-test.

The variability is assigned to true differences in calcium concentration because of undissolved oxide, not error in chemical analysis. The lowest calcium concentration observed is taken to be the upper limit of calcium (as CaO) solubility.

d. Conclusions

The solubility of Fe_2O_3 in a melt of 63% M_2CO_3-M_2SO_4 is approximately 0.18%. Solubility of CaO is not greater than 0.22%.

III. FILTRATION OF FLY ASH FROM MOLTEN SALTS

A. INITIAL STUDIES

1. Sintered Metal-and Tube Filter Tests

The first attempts to filter fly ash from molten salt were made with a sintered-metal disc welded to the end of a stainless steel tube. It was found that a sintered metal medium with pore diameter between 25 and 65 microns removed virtually all fly ash from suspension in molten carbonate.

2. Continued Sintered Metal-and Tube Filter Tests

As a part of measuring fly ash solubility in fused salts, suspension of ash in various melts were filtered with sintered-metal discs welded to 1 in. pipes.

Pure carbonate melt passed easily through the 10 micron sintered medium. However, melts containing sulfides, in a majority of attempts, could not pass through sintered metal with pore sizes up to 65 microns. Filters which had passed carbonate several times previously, would not allow sulfide at concentrations greater than 5% to pass. Similar difficulty was encountered in attempting to flow melts containing 25, 14, and 6 wt % sulfide through valves. Results indicate that there may be a solid phase, either a precipitate or solid corrosion products, which coats and blocks the medium's pores immediately upon contact. This necessitates that fly ash filtration in the Molten Carbonate Process occur upstream of the reduction reactor where sulfides are formed.

B. FILTRATION OF FLY ASH FROM MELTS WITH COMMERCIAL FILTERS

1. Apparatus and Procedure

The filter tested was a Ful-Flo cartridge-type, sintered stainless steel element with 10 micron pores, manufactured by Commercial Filters Corp. The apparatus consisted of a melt tank containing the molten salt, a regulating valve, the filter, a pressurization line to the melt tank, and associated plumbing and electrical heating. The apparatus is shown in Figure 2.

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Figure 3. The Sintered Metal Filter Housing and Filter Element with a Deposit of Frozen Fly Ash Cake

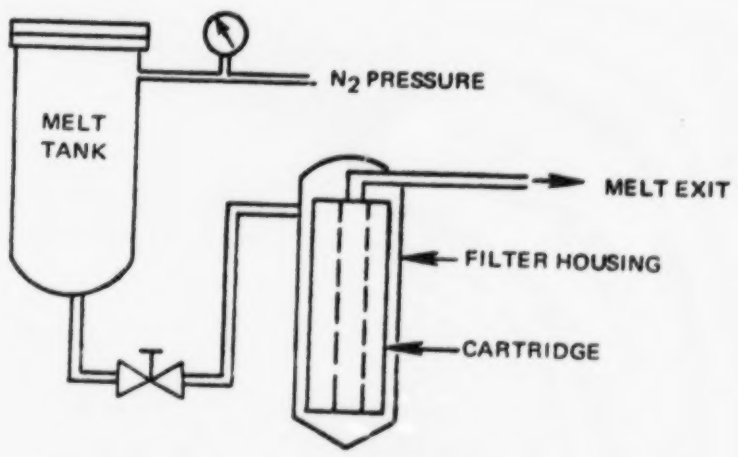

Figure 2. Filter Test Apparatus

The melt tank was filled with 10 kg of carbonate mixture and heated to 875°F. The tank was pressurized to 10 psig, the regulator valve opened, and the filtrate collected in a stainless steel beaker. About 4 kg of molten carbonate was run through the filter. The melt tank was then replenished with 10 kg of carbonate, and 150 g of fly ash (Colorado Public Service #1) was added. The melt tank was pressurized with nitrogen and the molten salt was caused to flow through the filter. A series of samples of filter effluent was taken and assayed for fly ash. The salt was reacted with a 30% hydrochloric acid solution and the remaining aqueous solution filtered in a Gooch filter. The Gooch filters were ignited at 850°F for one-half hour and weighed.

The filter with the cap removed and casing cut away is shown in Figure 3.

When the filtration was completed, the filter was opened and samples of the frozen filter cake were collected. The samples were powdered and

quartered. Two quarters were assayed for the percent carbonate in the cake. The other two quarters were dissolved in water and solids, filtered from the suspension, were dried and weighed, giving values for the percent fly ash in the cake.

2. Results

TABLE 10

DATA FROM EVALUATION OF THE SINTERED-METAL FILTER WITH AN ASH-MELT SUSPENSION

Run #	Time in Minutes	Total Salt Passed (g)	Rate (3)/(1) (g/min)	Mass Ash in Filter	ΔP psi	wt Sample (g)	wt Ash in Sample (g)	% Ash in Exit Salt
no ash	1/3	4000	1200	-	10	-	-	-
1	1	1056	1056	15.8	4	30.7071	0.000	0.00
2	1	1256	300	18.8	4	50.4848	0.0015	0.0030
3	2	1816	280	27.2	4	59.9917	0.0012	0.0020
4	2	2136	160	32.0	4	37.1587	0.0006	0.0016
5	4	2981	211	44.7	4	22.5891	0.0006	0.0027
-	1	5811	2830	87.2	8	-	-	-
6	1	6978	1167	-	8	21.7121	0.0001	0.0005

Results of the assays for carbonate and fly ash in the filter cake are listed in Tables 11 and 12.

TABLE 11

PERCENT CARBONATE IN THE FILTER CAKE SAMPLES

Replication	Treatment, cm from edge of filter		
	3	6	9
1	62.9	68.9	65.8
2	67.4	67.7	68.3

TABLE 12

PERCENT FLY ASH FOUND IN THE FILTER CAKE SAMPLES

Replication	Treatment, cm from edge of filter		
	3	6	9
1	27.9	30.3	28.8
2	28.0	28.8	28.4

The only materials in the filter system were carbonate and fly ash, so the frozen fly ash cake could have comprised only carbonate and ash. The means of 66.8 wt % carbonate and 28.7 wt % ash add up to only 95.5 wt %, perhaps indicating that part of the fly ash dissolved in the water wash.

The collection of frozen ash-salt cake from three locations on the filter was interpreted as three separate treatments. A completely randomized analysis of variance of the data showed that the composition of filter cake was independent of location on the filter element.

3. Discussion

One expects a filter flow resistance to increase as the cake builds up. The following development relating pressure loss across the filter to ash accumulation is founded on the assumptions of an incompresible cake and linear laminar flow through the cake and filter.

Darcy's law [4], which relates fluid flow velocity through a porous medium to pressure gradient and medium properties, can be written

$$\phi = K \frac{\Delta P}{L}$$

where ϕ is the flux of the fluid (grams/cm^2 sec), ΔP is pressure difference measured across a length L, and K is the so-called permeability coefficient (= 1 g-cm/dyne-sec). Replacing L by $\mathcal{V}/A$, volume of filter cake per unit area gives

$$\phi = K \frac{\Delta P_a}{\mathcal{V}/A}$$

The subscript "a" denotes ash, this being the ΔP across the fly ash cake. Assuming an incompressible (*) cake implies

$$1/\mathcal{V} = \rho_a/m_a$$

where ρ_a is cake density, and m_a is mass of ash on the filter. Combining the last two equations gives

$$\phi = K \frac{\Delta P_a}{\frac{m_a}{\rho_a A}} = \frac{\Delta P_a}{\Omega\sigma}$$

Here, $\Omega = (\rho_a/K)^{-1}$ is the cake resistivity and $\sigma = m_a/A$ is the cake loading, grams of cake/cm^2 of filter area. The pressure drop across the filter medium, ΔP_f, is related to flux of liquid through the filter by

$$\Delta P_f = \phi R_f$$

where R_f is the filter resistance. Combining the last two equations yields

$$\frac{\Delta P}{\phi} = \frac{\Delta P_a + \Delta P_f}{\phi} = R_f + \Omega\sigma$$

This suggests that the ratio of total pressure across a filter to the fluid flux varies linearly with cake loading.

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*If the cake were compressible, it would compact as ash accumulated on the filter. K, in turn, would decrease, invalidating Darcy's law, σ.

The data for flow through the 10 micron Ful-Flo filter have been plotted on $\Delta P/\phi$-σ coordinates in Figure 4.

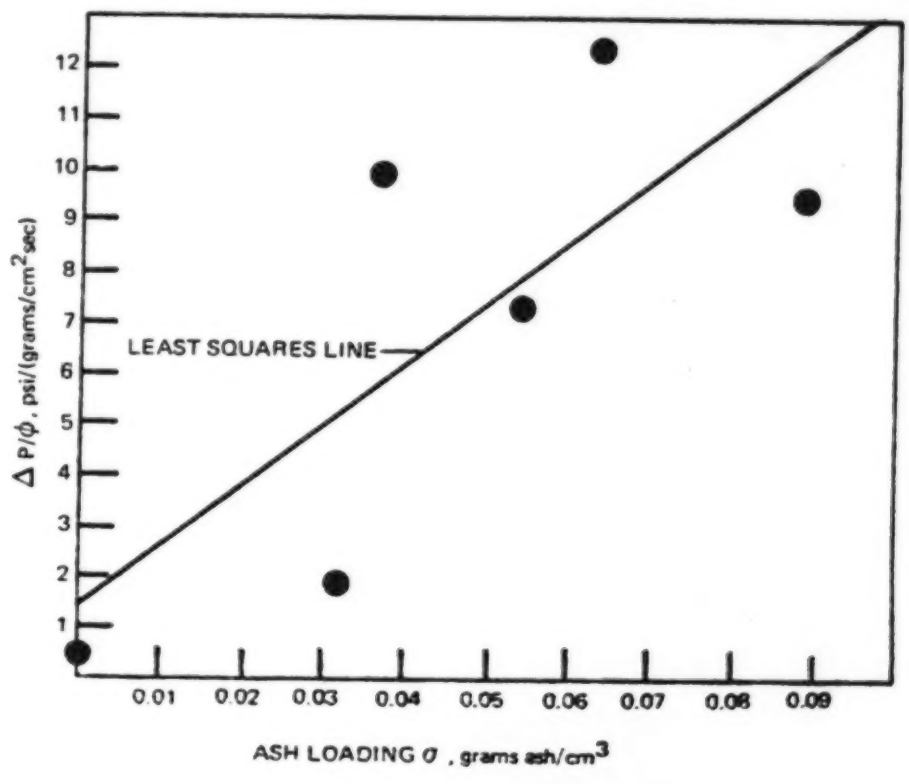

Figure 4. Variation of Pressure Drop With Coke Buildup During Filtration

The least squares line of the form $y = ax + b$ or $\Delta P/\phi = \Omega + R_f\sigma$ yields values of $\Omega = 120.1$ psi cm^2 sec/gm, a property of the sintered metal and melt only. These values allow prediction of pressure drop for a given flux and ash loading.

The results further reveal that the fraction of ash passing through the filter decreases with cake buildup. Under the assumption that the rate of filtration of ash particles by the ash cake is proportional to the flux and concentration of ash particles one may write

$$\% \text{ passing filter} = 1 - \% \text{ removal} = \exp\left(-\frac{\sigma}{\lambda} - \alpha\right)$$

where λ is a constant characterizing the cake and is a constant which describes the efficiency of the sintered metal as an in-depth filter. The results in column 9 of Table III follow with values of $\alpha \approx 10$ and $\lambda \approx 0.1$ gm/cm^3. The observation of no ash in the effluent salt in Run 1 occurred because ash-free salt from the previous run was still present in the system.

4. Conclusions

1. Almost all of the resistance to flow through the filter was due to the fly ash cake.

2. The 10 micron filter removed virtually all of the fly ash in suspension. No more than 30 ppm of suspended ash was found in the filtrate.

3. The sintered-metal medium is adequate for filtering fly ash particles from suspension in M_2CO_3.

4. The efficiency of filtration increased with fly ash accumulation on the filter.

5. At constant pressure, the flow rate through the filter decreased with ash accumulation.

6. The filter cake remaining on the sintered metal filter contained 66.8 wt % M_2CO_3 and 28.7 wt % fly ash.

7. The composition of the cake did not vary with position on the sintered-metal filter element.

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